

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

(10)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 207 787  
A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 86305124.9

(51) Int. Cl. 4: **C10M 117/02**, H01B 3/18 ,  
//(C10N10/06,70:00)

(22) Date of filing: 01.07.86

(30) Priority: 01.07.85 DE 3523473

(43) Date of publication of application:  
07.01.87 Bulletin 87/02

(84) Designated Contracting States:  
CH FR GB IT LI NL SE

(71) Applicant: **MINNESOTA MINING AND  
MANUFACTURING COMPANY**  
3M Center, P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)

(72) Inventor: Gunther, John Minnesota Mining  
and  
Manufacturing Co. 2501 Hudson Road P.O.  
Box 33427  
St. Paul Minnesota 55133-3427(US)

(74) Representative: Baillie, Iain Cameron et al  
c/o Ladas & Parry Isartorplatz 5  
D-8000 München 2(DE)

(54) Industrial gelling agent for hydrophobic organic liquids.

(57) Industrial gelling agent for hydrophobic organic liquids, particularly mineral oil or the like, on the basis of organic poly-oxo-aluminum salts of fatty acids and organic reactants reacting therewith, particularly reactants having hydroxyl or carboxyl groups, characterized in that the gelling agent is a solid matter obtained by the reaction of correspondingly selected poly-oxo-aluminum salts and reactants.

**EP 0 207 787 A2**

## INDUSTRIAL GELLING AGENT FOR HYDROPHOBIC ORGANIC LIQUIDS

The invention relates to industrial gelling agents, a method for the preparation of such gelling agents, and a method for impregnating electrical devices.

Hydrophobic organic liquids, particularly mineral oil or the like, are frequently used as impregnating agents, because of their water-repellant and electrically insulating properties, for instance for paper-insulated electrical cable, and/or as a filler material, for instance in cable connections, electrical transformers and the like. In this connection, it is particularly advantageous that the liquid state of aggregation makes it possible to completely fill a given space without leaving cavities which can be deleterious particularly in electrical installations. Furthermore, it is an advantage that many hydrophobic organic liquids have the property to creep even into smallest interstices. On the other hand, the use of a liquid as an impregnating or filling material requires a complete tightness of the enclosure into which the liquid is filled. This requirement often creates difficulties in practice. To circumvent these difficulties, it is known in the prior art to employ liquids which are solid at normal temperature and accordingly must be employed at elevated temperatures. In practical application, it is inconvenient to work at elevated temperatures and to provide therefore corresponding heating devices. Upon cooling-down, the liquid transforms into a solid mass which is no longer or still only slightly deformable; this is undesirable in several cases. Therefore, also the use of industrial gelling agents has been reported which are added to the liquid and after a certain time form with the latter a gel which no longer can flow out through leaks and remains deformable. Known gelling agents of this kind contain organic aluminum compounds, particularly poly-oxo-aluminum compounds, and react with hydroxyl or carboxyl groups to form a thixotropic gel. In this manner, for instance, paints are provided with a, typically, desirable thixotropic property. Poly-oxo-aluminum compounds of the kind indicated are distributed, for instance, by the British company Manchem Ltd.

Frequently, hydrophobic organic liquids, particularly mineral oil or the like, do not comprise hydroxyl or carboxyl groups so that the said gelling agents cannot react directly with these liquids. This is particularly the case in all electrical applications because impregnating and filling materials used therefor shall not contain, as a rule, hydroxyl or carboxyl groups. In such cases, therefore, a reactant, mostly in the form of a liquid, which contains the groups necessary for the gelling reaction was additionally added upon the addition of the organic

aluminum compound. For instance, solvents are suitable as reactant which contain hydroxyl or carboxyl groups. In practical application, it is inconvenient to additionally add the reactant. Also, dosing errors may easily happen. Added thereto is the difficulty that the said organic aluminum compounds react very strongly with moisture and thus must be stored and shipped under an air-tight seal and must be handled with great care.

In the course of the gelling reaction, the reactive groups of the reactant are converted into electrically unobjectionable compounds, whereby the insulating properties of the liquid improve gradually to the original value. This can be observed from the increase of the dielectric loss factor which can be easily measured. Normally, it will last several days until the electrical insulating properties of the gelled liquid have improved so far that an operational electrical load is again possible. This long waiting time until the respective devices are put into operation is very inconvenient and causes considerable costs and waste times.

It is the object of the invention to provide an industrial gelling agent particularly for electrical applications, which is more conveniently applicable and makes possible to shorten the aforescribed waiting times.

Briefly, the present invention provides an industrial gelling agent for hydrophobic organic liquids, particularly mineral oil or the like, on the basis of organic poly-oxo-aluminum salts of fatty acids and reactants reacting therewith, particularly reactants having hydroxyl or carboxyl groups, characterized in that the gelling agent is a solid matter obtained by reaction of correspondingly selected poly-oxo-aluminum salts and reactants.

In another aspect, a method is provided for preparing an industrial gelling agent for organic liquids immiscible with water, particularly mineral oil or the like, on the basis of organic poly-oxo-aluminum salts of fatty acids and organic reactants reacting therewith, particularly reactants having hydroxyl or carboxyl groups, characterized by reacting a correspondingly selected poly-oxo-aluminum salt of a fatty acid with the reactant to a solid reaction product forming the gelling agent, and optionally comminuting the product.

In still another aspect, a method is provided for impregnating electrical devices, particularly cable connections, with an electrically non-conductive organic liquid, particularly mineral oil or the like, the method comprising providing the liquid with an added gelling agent in a cavity provided in the device, characterized by using a solid powder-like gelling agent as described above.

The industrial gelling agent of the present invention is a solid matter which is the result of a reaction of the poly-oxo-aluminum salts and the reactants. It has been found that the industrial gelling agent according to the invention obviously because of its property as being a reaction product, is insensitive towards moisture and can be easily handled and stored, and will cause the desired gelling in a very short time after being added to the liquid to be thickened which need not contain groups capable of reacting with poly-oxo-aluminum salt, the electrical insulating properties of the obtained gel permitting to apply immediately an electrical load to the gel, thus putting the respective electrical device into operation. The gelling agent according to the invention is an almost inert solid matter which can be stored and handled without particular precautions. Preferably, the gelling agent according to the invention is pulverized. Then, it need only be sprayed or intermixed into the liquid to be gelled, whereupon the gelling takes place within a comparably very short time, for instance one hour. Through suitable selection of the poly-oxo-aluminum salt and the reactant, powder-like gelling agents can be obtained which are capable of effecting in mineral oil a gelling time of less than one hour.

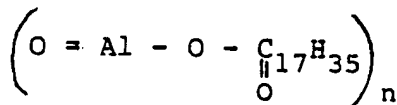
With the gelling agent according to the invention, the reaction time needed for the reaction between the poly-oxo-aluminum salt and the reactant obviously is transferred into the preparation of the gelling agent because, normally, this reaction requires a reaction time of several hours at elevated temperatures of particularly 120°C. In the preparation of the gelling agent according to the

invention, these reaction conditions are not disadvantageous. Decisive and surprising is the fact that in practical application, only a very short gelling time is necessary.

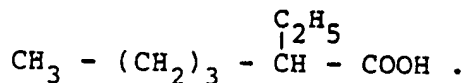
More particularly, it is possible to determine, by few experiments, pairs of poly-oxo-aluminum salts and reactants with which the gelling agent prepared therefrom in accordance with the invention is capable of effecting a gelling time in mineral oil of below 10 minutes. In this connection, it is also of importance that in practical application, the gelling time is dependent upon the particle size of the solid matter gelling agent according to the invention. Therefore, a particle size corresponding to a desired gelling time can be selected, with smaller particle sizes corresponding to short gelling times.

In the application of the gelling agent according to the invention, it is not necessary to elevate the temperature. It suffices to intermix the gelling agent with the liquid at room or ambient temperature. No further substances like solvents and the like need be added; accordingly, also all problems encountered with such additional materials with respect to storage and environmental pollution are dispensed with. The gel obtained with insulating oils, for instance hydrocarbon oils has good electrical insulating properties already shortly after its preparation, whereby the device in which this gel is provided can be put into operation without delay. The gel has a very good temperature resistivity and can be maintained free of decomposition at temperatures of at least about 150°C.

Particularly advantageous properties is provided by a gelling agent, according to the invention, which has been obtained by an essentially stoichiometric reaction of poly-oxo-aluminum stearate of the formula



with 2-ethyl hexanoic acid of the formula



This gelling agent has a density in the range of the density of the liquids usually to be gelled, as for instance mineral oil. The density can be set within a certain range in accordance with the degree of polymerization of the organic aluminum salt. For instance, the density can be slightly greater than the density of the liquid to be gelled. This is advantageous particularly upon the intermixing. For instance, the density can be about 0.97 g/cm<sup>3</sup>.

The preparation of the industrial gelling agent according to the invention is characterized by reacting a correspondingly selected poly-oxo-aluminum salt of a fatty acid with the reactant to a solid reaction product forming the gelling agent, and possibly comminuting the product. Thus, only simple operational steps are necessary for the preparation.

In order that the gelling agent obtained as a solid reaction product does not have disturbing alien properties, it is appropriate to react the poly-oxo-aluminum salt essentially completely with a stoichiometric amount of the reactant.

It has been found that the reaction proceeds particularly rapidly if a reactant is used which is substituted with low hydrocarbon radicals, preferably having five or less atoms, particularly a liquid reactant in the form of an organic acid substituted with low hydrocarbon radicals. As the organic acid, appropriately a low alkanolic acid, having up to ten carbon atoms and preferably having five to ten carbon atoms, particularly ethyl or propyl hexanoic acid, is used. The reactant 2-ethyl hexanoic acid has been found to be particularly useful in practice.

The reaction between the poly-oxo-aluminum salt and the reactant is performed appropriately at about 100 to 140°C, preferably at about 120°C. Then, a smooth reaction is obtained in a short reaction time and without the danger of decomposition.

The application of the gelling agent according to the invention is very simple and offers particular advantages in the impregnation of electrical devices, particularly cable connections, with an electrically non-conductive organic liquid, particularly mineral oil or the like, wherein the liquid including the added gelling agent is disposed in a cavity provided in the device. In accordance with the invention, a solid, powder-like gelling agent according to the invention is used for this purpose. For instance, the gelling agent can be sprayed or filled

into the cavity which is already filled with the liquid. However, a method is particularly advantageous in which the gelling agent is added to the liquid prior to the introduction thereof into the cavity; in accordance with the invention, the gelling agent is added to the liquid immediately prior to the introduction of the latter into the cavity. Then, the mixture remains sufficiently long of low viscosity to be able to creep, like the liquid, into all cavities and interstices.

It should be particularly noted that not any combination of an organic aluminum compound and a carboxylic acid will result in a gelling agent. If, for instance, instead of the above-described reaction between poly-oxo-aluminum stearate and the 2-ethyl hexanoic acid, a reaction is conducted between the same aluminum compound and stearic acid, also a solid matter product will be obtained. However, when that product is comminuted to form a powder, and the powder is intermixed at room temperature with mineral oil, a gel will not be formed. If, however, the aluminum salt and the stearic acid is intermixed prior to the reaction with the mineral oil, and the mixture is held for three to four minutes at 120°C, a gel will be formed. Thus, it is necessary, when deviating from the presently stated examples, to determine suitable reactants for the employed organic aluminium salt individually by experiments.

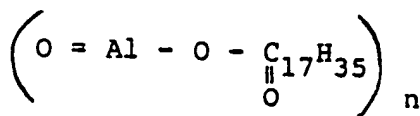
## Claims

1. An industrial gelling agent for hydrophobic organic liquids, particularly mineral oil or the like, on the basis of organic poly-oxo-aluminum salts of fatty acids and reactants reacting therewith, particularly reactants having hydroxyl or carboxyl groups, characterized in that the gelling agent is a solid matter obtained by reaction of correspondingly selected poly-oxo-aluminum salts and reactants.

2. An agent according to claim 1 wherein said reactant is a low alkanolic acid having up to 10 carbon atoms.

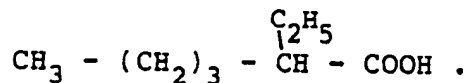
3. The composition according to claim 2 wherein said alkanolic acid comprises 5 to 10 carbon atoms.

4. An agent according to claim 1, obtained by essentially stoichiometric reaction of poly-oxo-aluminum stearate of the formula



with 2-ethyl hexanoic acid of the formula

10



5. An agent according to claim 4, characterized in that it has a density in the range of the density or slightly greater than the density of the liquid to be gelled.

6. An agent according to any one of the preceding claims, characterized in that it is pulverized.

7. An agent according to claim 6, characterized in that its particle size is selected in correspondence with the desired gelling time, with smaller particle sizes corresponding to shorter gelling times.

8. An agent according to any one of the preceding claims, characterized in that it is capable of effecting a gelling time in mineral oil of less than one hour due to a corresponding selection of the poly-oxo-aluminum salt and the reactant.

9. A method for preparing an industrial gelling agent for organic liquids immiscible with water, particularly mineral oil or the like, on the basis of organic poly-oxo-aluminum salts of fatty acids and organic reactants reacting therewith, particularly reactants having hydroxyl or carboxyl groups, characterized by reacting a corresponding selected poly-oxo-aluminum salt of a fatty acid with the reactant to a solid reaction product forming the gelling agent, and optionally comminuting the product.

10. A method according to claim 9, characterized by reacting the poly-oxo-aluminum salt essentially completely with a stoichiometric amount of the reactant.

11. A method according to claim 10, characterized by using a liquid reactant in the form of an organic acid substituted with low hydrocarbon radicals.

12. A method according to claim 11, characterized by using as the reactant, a low alkanolic acid substituted with low hydrocarbon radicals.

13. A method according to claim 10 characterized by using ethyl or propyl hexanoic acid as the reactant.

14. A method according to claim 10, characterized by using 2-ethyl hexanoic acid as the reactant.

15. A method according to any one of the preceding claims, characterized by performing the reaction at about 100 to 140°C.

16. A method for impregnating electrical devices, particularly cable connections, with an electrically non-conductive organic liquid, particularly mineral oil or the like, the method comprising providing the liquid with an added gelling agent in a cavity provided in the device, characterized by using a solid powder-like gelling agent according to claim 5.

17. A method according to claim 16, comprising adding the gelling agent to the liquid prior to introducing the latter into the cavity, characterized by adding the gelling agent to the liquid immediately prior to introducing the latter into the cavity.

50

55

5

**EUROPEAN PATENT APPLICATION**

Application number: 86305124.9

Int. Cl.4: **C10M 117/02** , H01B 3/18 ,  
/(C10N10/06,70:00)

Date of filing: 01.07.86

Priority: 01.07.85 DE 3523473

Date of publication of application:  
07.01.87 Bulletin 87/02

Designated Contracting States:  
CH FR GB IT LI NL SE

Date of deferred publication of the search report:  
10.08.88 Bulletin 88/32

Applicant: MINNESOTA MINING AND  
MANUFACTURING COMPANY  
3M Center, P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)

Inventor: Gunther, John Minnesota Mining  
and  
Manufacturing Co. 2501 Hudson Road P.O.  
Box 33427  
St. Paul Minnesota 55133-3427(US)

Representative: Baillie, Iain Cameron et al  
c/o Ladas & Parry Isartorplatz 5  
D-8000 München 2(DE)

Industrial gelling agent for hydrophobic organic liquids.

Industrial gelling agent for hydrophobic organic liquids, particularly mineral oil or the like, on the basis of organic poly-oxo-aluminum salts of fatty acids and organic reactants reacting therewith, particularly reactants having hydroxyl or carboxyl groups, characterized in that the gelling agent is a solid matter obtained by the reaction of correspondingly selected poly-oxo-aluminum salts and reactants.

**EP 0 207 787 A3**



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 86 30 5124

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X A	EP-A-0 029 589 (CHATTEM, INC.) * The whole document *	1-3, 6, 7 , 12 4, 5, 13- 15	C 10 M 117/02 H 01 B 3/18 // C 10 N 10/06 C 10 N 70/00
X A	GB-A- 825 878 (HARDMAN & HOLDEN LTD.) * The whole document *	1, 6-10  2-5, 11- 17	
X A	FR-A-1 535 153 (ESSO) * The whole document *	1, 9	
	GB-A- 530 374 (CALLENDER'S CABLE & CONSTRUCTION CO., LTD.) * Claims; page 2, lines 10-18 *	16, 17	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 M H 01 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-05-1988	Examiner DE LA MORINERIE B.M.S.E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P0401)